

Implementation of Catalytic Technologies for Mitigation of Humid, Lean Methane Exhaust Streams; Technological Hurdles for Industrial Implementation

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Significance and Relevance

The current study examines the development of catalytic technology and its potential to reduce anthropogenic, fugitive greenhouse emissions with a focus on the difficulties associated with implementing catalytic technologies in commercial applications. Specifically, an understanding of catalyst activity and mechanisms of deactivation is crucial for the development of a system which exhibits the stability necessary for industrial applications.

Preferred and 2nd choice for the topic: Air cleaning and combustion; Automotive and stationary emission control.

Preferred presentation: Oral only

Introduction and Motivations

An increased need to minimize fugitive greenhouse gas (GHG) emissions has put pressure on industries to reduce their associated emissions, in some instances deemed a necessary requirement to maintain financial viability. Recently, methane has gained attention due to its significantly higher global warming potential¹, leading to the development of systems to mitigate fugitive emissions, particularly those associated with mining and stationary power generation. For mining applications, very low concentrations of methane (<1%) are emitted in the ventilation exhaust, with very high flowrates ($100 - 600 \text{ m}^3/\text{s}$) contributing to approximately 70% of the GHG emissions associated with the sector. For these applications, catalytic technologies offer several advantages over traditional thermal methods, with a demonstrated ability to oxidize lower concentrations of methane, operate at much lower temperatures and demand considerably lower energy input and physical footprint.

Materials and Methods

The catalytic oxidation of lean methane streams was examined in a stainless steel, tubular, fixed bed micro-reactor. Ventilation air methane (VAM) streams were simulated using flows of methane (0.2 – 0.7%) in humidified air. Catalysts were prepared via incipient wetness before being dried at 110°C for 20 hours. Sized catalysts ($250 - 400 \mu m$) were calcined *in situ* at 500°C prior to reaction.

Results and Discussion

The industrial implementation of catalytic technology for emission control requires the catalyst to exhibit high levels of activity and stability. Palladium catalysts have been identified as highly active oxidation catalysts, however there is no clear agreement on the major cause for loss of catalytic activity, with several potential processes discussed in the literature. The presence of water vapor in the feed stream is often not considered, however previous studies have reported that water competes with metal sites, transforming active palladium oxide to less active palladium hydroxide.

The current study examines oxidation of lean, humid methane streams over palladium on various support materials. Supports with differing properties were used to examine the effect of varying characteristics in minimizing catalyst deactivation and enhancing stability. The results displayed in Figure 1 show a significant difference in catalyst stability. Pd/Al₂O₃ was used to compare results with a standard, industrial oxidation catalyst, while MFI-structured supports were used to examine variations in chemical characteristics.



Figure 1: Catalyst stability under synthetic VAM conditions at 460°C and 100,00 h⁻¹ GHSV. Feed composition 0.7% CH₄ in humidified air. Catalysts tested (1.2 wt% Pd); \bullet Pd/TS-1, \bullet Pd/Al₂O₃, \bullet Pd/ZSM-5 (SiO₂:Al₂O₃ = 50), \bullet Pd/ZSM-5 (SiO₂:Al₂O₃ = 23).

It is theorized that the differences in catalyst stability observed is a result of the varying presence of aluminum in the support framework, with increased AI content leading to a strong affinity for water vapor. It was observed that a decreased AI content results in a decreased concentration of Bronsted acid sites², which is proposed to inhibit hydroxyl accumulation on the catalyst surface³. It has been reported that this can also lead to an increased oxygen mobility, which can accelerate hydroxyl desorption, further impeding accumulation. This is further highlighted by the significant difference between the ZSM-5 catalysts, where increasing the SiO₂:Al₂O₃, thereby lowering associated Bronsted acid sites, greatly improved stability.

References

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